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PARTIALLY FLUORINATED LUBRICANTS FOR SOLID SURFACES

The invention relates to the use of partially fluorinated compounds as ski lubricants.

Ski waxes are used in order to enhance the sliding properties of skis. Conventional ski waxes generally include relatively high molecular mass hydrocarbons such as paraffins, fatty acids, fatty acid esters, and fatty alcohols or mixtures of these and similar compounds. Certain fluorinated compounds have proven extremely effective ski waxes and are employed particularly in the high-performance sport. The reason for the great effectiveness of fluorinated waxes is the coating of the ski with a fluorinated surface possessing very low surface tension, thereby greatly reducing the friction. By coating with fluorochemicals it is possible to lower the surface tension of, say, polyethylene (31 dyn/cm) to levels of 6-18 dyn/cm. The value of 6 dyn/cm is achieved for a surface composed of perfectly oriented CF3 groups.

Some fluorinated compounds which can be used as ski lubricants are already known. WO 89/10950, for example, describes the addition of PTFE micropowder to unfluorinated ski waxes. The molar weight of the PTFE is preferably 50 000-400 000 g/mol and the particle size is less than 15 μm. EP 0 132 879 describes the synthesis of relatively long-chain perfluoroalkanes of the formula $F(CF_2)_nF$ and also their use as lubricants for surfaces. EP 0 444 752 describes the use of fluorinated diblock compounds of the formula $F(CF_2)_n$-$(CH_2)_mH$, where n = 3-15 and m = 5-23, as ski wax. These compounds have the advantage of compatibility with unfluorinated paraffin waxes, owing to the hydrocarbon block. DE 4 139 765 describes oligomers of fluorinated olefins of the formula $F(CF_2)_n$-$CH=CH_2$. The product can be prepared by free-radical oligomerization of said olefins and is suitable as a lubricant for a variety of surfaces. US 5,502,225 and DE 100 29 623 describe fluorinated oligomeric urethanes which are obtained by addition reaction of fluorine-free isocyanates and fluorinated alcohols as essential components. EP 0 421 303 describes the use of partially fluorinated polyacrylates. The preparation takes place by free-radical copolymerization of fluorinated acrylates such as 2-perfluoroalkylethyl acrylate, for example, with nonfluorinated monomers such as long-chain fatty alcohol acrylates, for

example. Ski waxes may also be provided with a variety of additives in order to prevent the friction-induced electrostatic charging, which can lead to the adherence of a water film. CH 660 018, for example, describes the use of graphite for the purpose of increasing the conductivity.

It has now been found that certain partially fluorinated compounds can surprisingly likewise be used as ski waxes. These compounds are coupling products of one or more perfluoroalkyl radicals with a fluorine-free alkyl or aryl radical. Apart from oxygen atoms in the form of ether bonds, the coupling product must be composed exclusively of the elements fluorine, carbon, and hydrogen. Absent an ether bond, the fluorine-free alkyl or aryl radical must have at least one monocyclic or polycyclic structural element, which may be saturated, unsaturated, aromatic, possibly branched, and monofunctional or bifunctional.

The invention provides lubricants intended for solid surfaces and comprising a partially fluorinated compound of formula 1

$$RF\text{-}(A)_a\text{-}(O)_b\text{-}(B)_c\text{-}(D)_d\text{-}(RF)_e \qquad (1)$$

where
RF is a perfluorinated radical of formula $F(CF_2)_n$-,
n is a number from 1 to 20;
A is C_1-C_{30}, preferably C_1-C_{18}, alkylene.
B is arylene having 6 to 14 carbon atoms or is a saturated or unsaturated monocyclic or polycyclic hydrocarbon having 3 to 30, preferably 3 to 18 carbon atoms,
D is hydrogen or C_1-C_{30}, preferably C_1-C_{18}, alkyl,
a is zero or 1,
b, c, and d are zero, 1 or 2 and e is zero or 1, with the proviso that b and c are not simultaneously zero.

Preference is given to compounds of the above formula in which a = 1, b = 0, c = 1, d = 1, D = H, and e = 0, the remaining symbols having the definitions given above.

The compounds of formula above can be synthesized in principle in a number of ways. The most common is the addition reaction of

perfluoroalkyl iodides with olefinic double bonds, free-radically or metal-catalyzed, for example, and substitution reaction of perfluoroalkyl iodides on aromatic systems, which are carried out with metal catalysis, for example. It will be appreciated that other methods, not specified here but sufficiently well known to the skilled worker, of linking perfluoroalkyl radicals to fluorine-free compounds are also possible.

Surprisingly it has now been found that the compounds described above are outstandingly suitable for coating skis for the purpose of improving the sliding properties. The effect is presumably attributable to the fact that the fluorine radicals orient themselves toward the air and, as a result of the CF_3 surface coating thus formed, a low-energy surface is produced which has a very low surface tension and also good sliding properties.

The requirements imposed on the physical and chemical properties of a ski wax differ greatly according to snow and weather conditions. Through a suitable choice of the fluorinated moiety and of the fluorine-free moiety of the active compound it is readily possible to vary the physicochemical properties of the active compound within wide limits and to adapt them to the requirements. It is also possible to use combinations of two or more of the active compounds described. Long-chain perfluoroalkyl radicals $\geq C_8F_{17}$, for example, increase the hardness of the active compound. As a result of the fluorine-free moiety present, moreover, it is possible to achieve miscibility or compatibility with fluorine-free ski waxes.

The compounds described can be applied in conventional manner to the sliding surface of the ski, by means for example of the melting of these compounds, where present in solid form, with a hot iron and their application to the ski. As alternative to this the compounds described can be applied in the form of a solution in one or more organic solvents, preferably in a concentration of 0.5% - 5%, or in the form of a solid, to the ski. Where the wax is used in the form of a solution it is necessary to select a suitable solvent, depending on the fluorine content. At high fluorine content it may be necessary to use fluorinated solvents such as perfluorohexane, 1H-perfluorohexane or Frigen products, for example. At a low fluorine content, nonfluorinated solvents are suitable as well, such as ethyl acetate, butyl acetate or THF, for example. It is also possible to use mixtures of two or more solvents. A further possibility is to employ the

active compound in the form of a suspension or dispersion. The fluorinated compounds described can be combined, alone or in a mixture, with other fluorinated or nonfluorinated ski waxes.

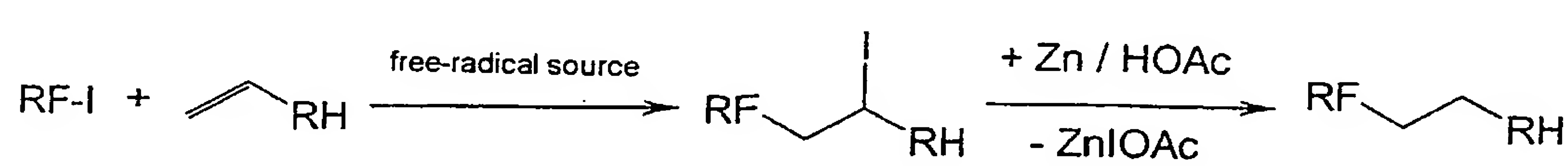
The fluorinated active compounds described are suitable not only as ski waxes but also for coating surfaces of a wide variety of kinds such as metal, plastic, and glass, for example. The coating applies a hydrophobic and oleophobic film to the surface in question, and said film greatly reduces the friction.

Examples

Synthesis

Compounds 1-6 were synthesized by free-radical addition reaction of perfluoroalkyl iodide with C-C double bonds and subsequent hydrodehalogenation, in accordance with reaction scheme I and the following general instructions.

Reaction scheme I:



General instructions for the synthesis of compounds 1-6:
Perfluoroalkyl iodide and olefin component are reacted in a molar ratio of 1:1 with 5 mol% of percarbonate and/or peroxide free-radical initiator (e.g., dilauryl peroxide) at 100-110°C for 2 h. Then a further 5 mol% of free-radical initiator are added and reaction continues at 100-110°C for 2 h. After the reaction mixture has cooled to room temperature, 1.5 times the mass of isopropanol, 0.5 times the mass of acetic acid, and 150 mol% of zinc powder are added and the mixture is stirred for 1 h. Reaction then takes place under reflux conditions for a further 3 h. Following filtration to remove insoluble fractions, the solvent is stripped off and the residue is freed under a high vacuum from unreacted starting materials and byproducts. The purity of the product is between 85% and 95%.

Synthesis of compound 7

Compound 7 was prepared in accordance with a set of instructions from J. Org. Chem. 6, (2002), 7185-7192 by coupling 2 mol of RFI and one mole of biphenyl with copper in DMSO as solvent.

Synthesis of compound 8

Compound 8 was prepared by a set of instructions from Organikum, Wiley-VCH, 21st edition, 2001, p. 375 by Friedel-Crafts alkylation of perfluoroalkylpropyl chloride (prepared by reacting 3-perfluoroalkyl-1-propanol and thionyl chloride) and decylbenzene, with catalysis by aluminum chloride.

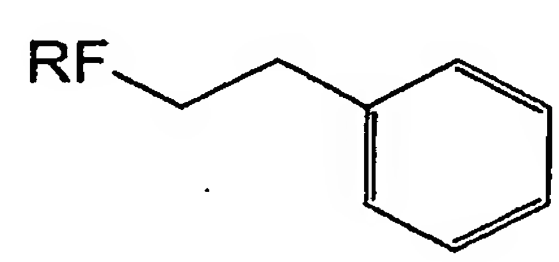
Synthesis of compound 9

Compound 9 was prepared by a set of instructions following the general procedure of Organikum, Wiley-VCH, 21st edition, 2001, p. 239 by reacting perfluoroalkylpropyl tosylate (prepared by reacting 3-perfluoroalkyl-1-propanol with p-toluenesulfonyl chloride) and dodecylphenol in acetone with potassium carbonate.

Examples

Compound 1:

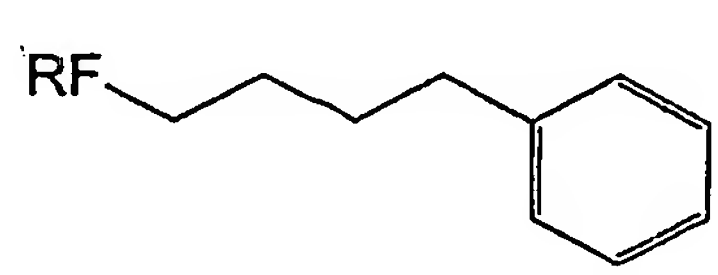
Product of RFI (RF = $F(CF_2)_n$, n = 63% 10, 30% 12, 7% ≥ 14) and styrene



1 RF-CH_2-CH_2-C_6H_5

Compound 2:

Product of RFI (RF = $F(CF_2)_n$, n = 63% 10, 30% 12, 7% ≥ 14) and 4-phenyl-1-butene



2 $RF-(CH_2)_4-C_6H_5$

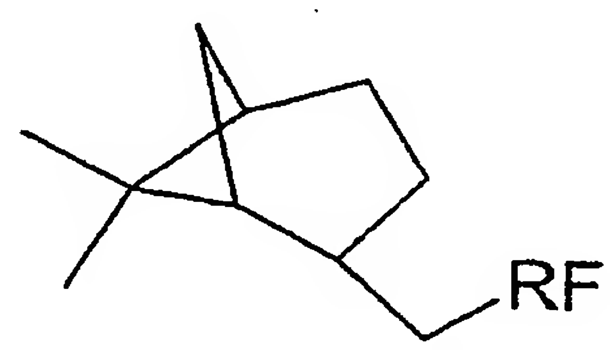
Compound 3:

Product of RFI ($RF = F(CF_2)_n$, n = 8) and 3-butenyl dodecyl ether

3 $RF-(CH_2)_4-O-C_{12}H_{25}$

Compound 4:

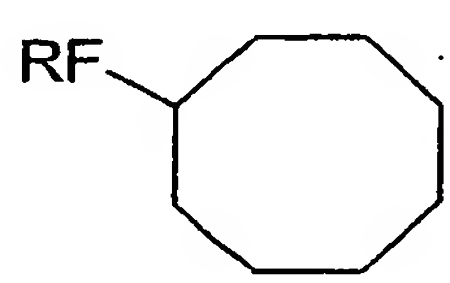
Product of RFI ($RF = F(CF_2)_n$, n = 63% 10, 30% 12, 7% ≥ 14) and β-pinene



4 RF-β-pinene

Compound 5:

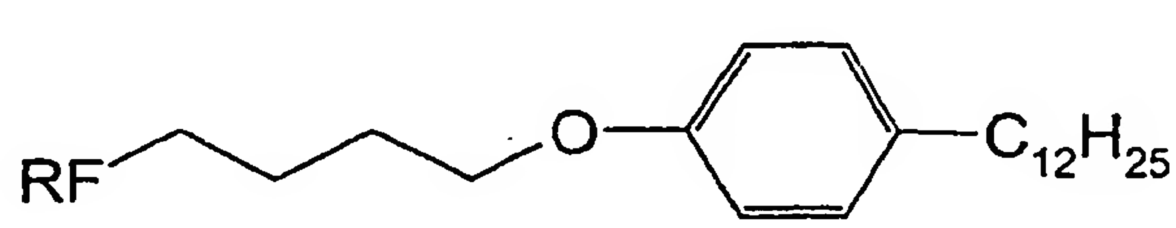
Product of RFI ($RF = F(CF_2)_n$, n = 63% 10, 30% 12, 7% ≥ 14) and cyclooctene



5 RF-cyclooctene

Compound 6:

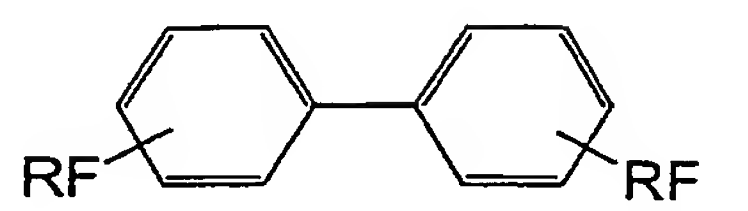
Product of RFI ($RF = F(CF_2)_n$, n = 8) and 3-butenyl dodecylphenyl ether



6 $RF-(CH_2)_4-O-C_6H_4-C_{12}H_{25}$

Compound 7:

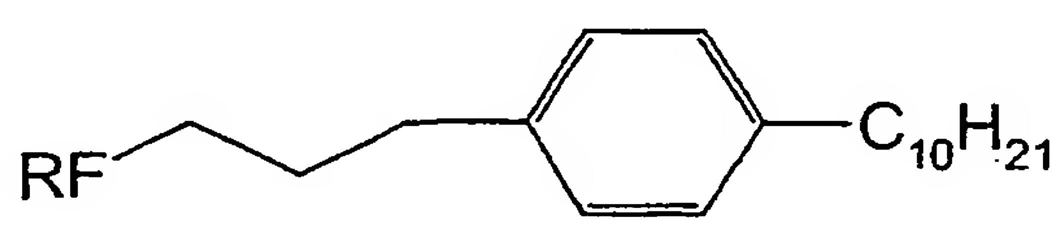
Product of 2 mol of RFI ($RF = F(CF_2)_n$, n = 8) and 1 mol of biphenyl



7 $RF-C_6H_4-C_6H_4-RF$

Compound 8:

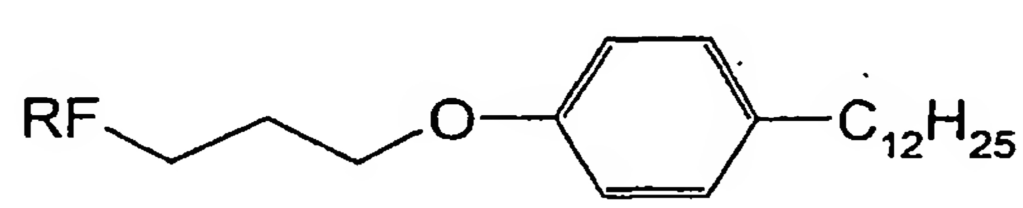
Product of perfluoroalkylpropyl chloride and decylbenzene ($RF = F(CF_2)_n$, n = 7% 6, 63% 8, 28% 10, 2% ≥ 12).



8 $RF-(CH_2)_3-C_6H_4-C_{10}H_{21}$

Compound 9:

Product of perfluoroalkylpropyl tosylate and dodecylphenol ($RF = F(CF_2)_n$, n = 7% 6, 63% 8, 28% 10, 2% ≥ 12).



9 $RF-(CH_2)_3-O-C_6H_4-C_{12}H_{25}$